

In-situ Diagnostics of Coupled Electrochemical-Mechanical Properties of Solid Electrolyte Interphases on Lithium Metal for Rechargeable Batteries

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Project ID # ES318

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2019
- Percent completed: 50%

Budget

- Total project funding: **\$1,815,845**
 - DOE share: \$1,452,676
 - Contractor share: \$363,169
- Funding received in FY2017: \$188,560
- Funding for FY2018: \$552,119

Barriers addressed

Li metal film electrodes with

- Low coulombic efficiency
- Dendrite growth
- Short calendar and cycle life

Partners

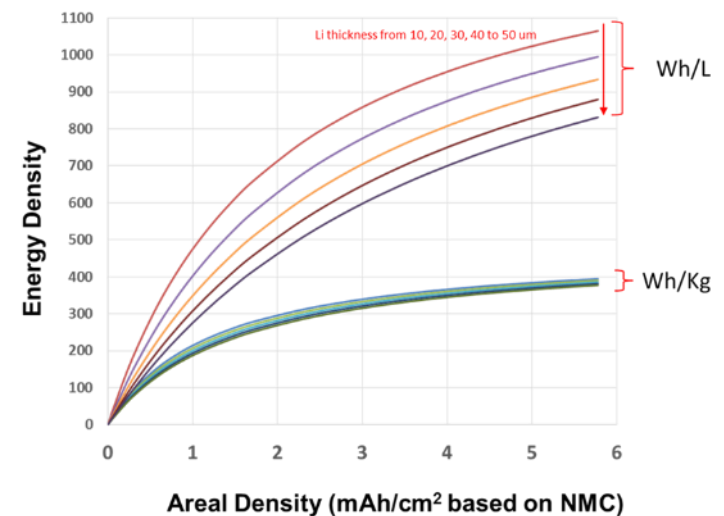
Interactions/ collaborations

- Brown University
- Michigan State University
- University of Kentucky

Project lead: General Motors

Relevance

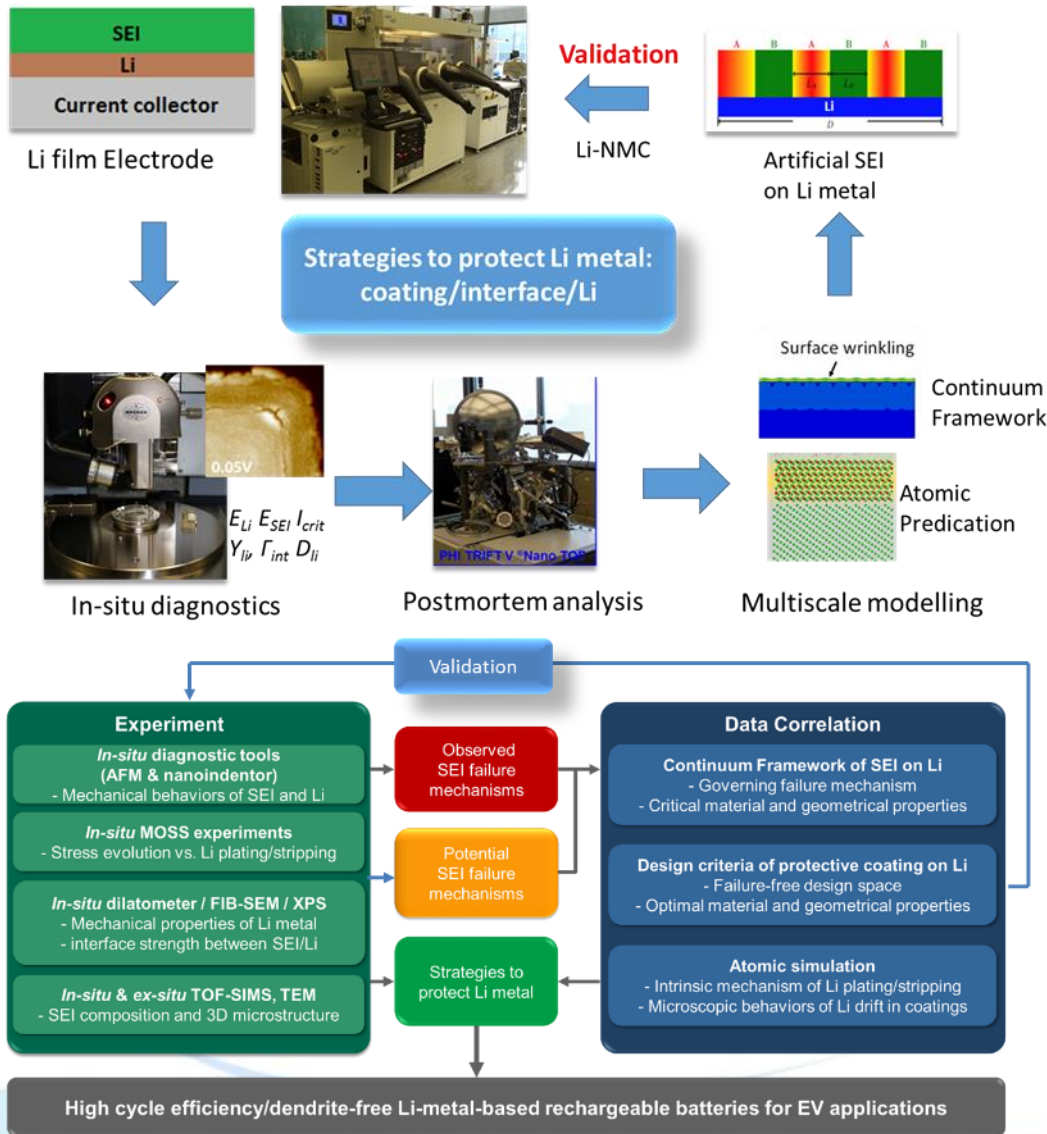
- Mechanical incompatibility between the SEI layers and the soft Li metal leads to SEI breakage during Li plating/stripping processes. **The mechanical characterization of an ultrathin SEI on a soft metal is a “grand challenge”.**
- The evolution of the Li surface morphology is also closely tied to non-uniform current distribution that depends on Li diffusion through the SEI and the Li plating/stripping kinetics. **Relationships between these processes and the interface mechanical integrity have not been studied in detail yet.**
- **The lack of a well-controlled system** that can be used to conduct fundamental investigations on the coupled mechanical/chemical properties of the SEI layer with Li metal in an electrochemical environment.
- Most academia research work use a large amount of excess lithium. It is **critical to precisely control Li loading for investigating the cycle efficiency with targeted energy density.**



Project Milestones

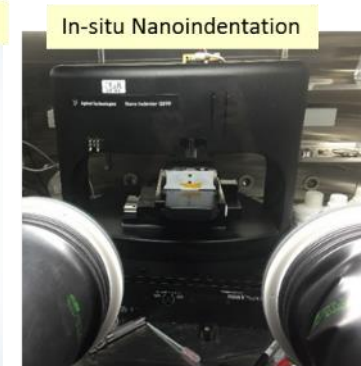
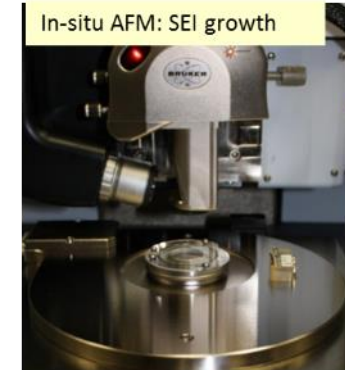
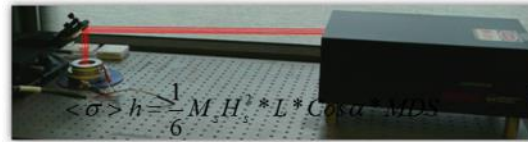
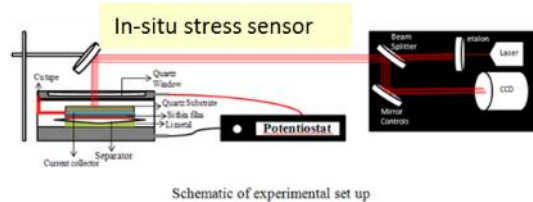
Month/ Year	Milestone of Go/No-Go Decision	Status
Dec. 2017	A continuum model of SEI growth to predict potential SEI failure modes.	completed
March 2018	The impact of Li deposition induced stress on Li morphology and cycle efficiency.	completed
June 2018	Interface adhesion energy calculations and the predication of where interface delamination will occur. Li plating kinetics at Li/single-component SEI/electrolyte interface predicted by MD simulation.	on track
Oct. 2018	Make Go/No-Go decision based on whether the property map is realistically achievable and practically useful for EV application.	on track

Approach/Strategy



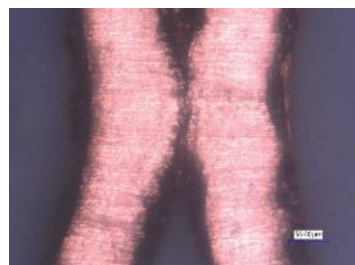
- Develop a model system and identify the critical mechanical/chemical/transport properties of SEI/Li electrode responsible for the failure.
- Establish a multi-dimensional property map to correlate SEI/Li mechanical failure, morphology, and cycle efficiency
- Establish a design guidance for developing the desirable artificial SEI layer to protect Li metal.

Accomplishment 1: Established experimental capability for developing model system and in-situ diagnostics

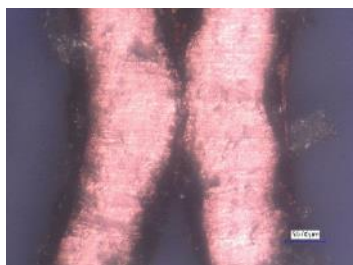


- Developed Li film electrodes with controlled capacity and protective coatings as artificial SEI layer;
- Established comprehensive *in-situ* electrochemical diagnostic techniques to investigate mechanical behavior of SEI and Li electrode.

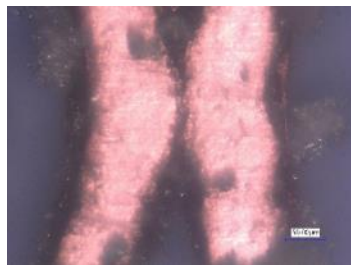
Accomplishment 2: Identified the impact of electrolytes on Li plating and stripping (dendrite growth, morphology evolution, and SEI composition)



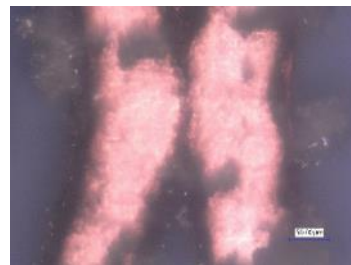
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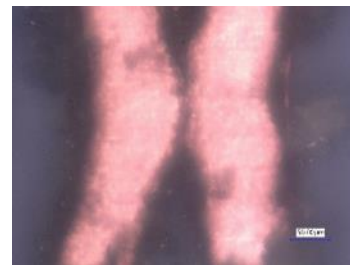
Plating



Plating



Plating

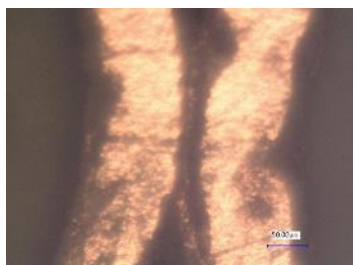


After Stripping

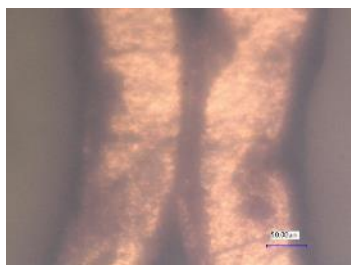
In carbonate based electrolyte



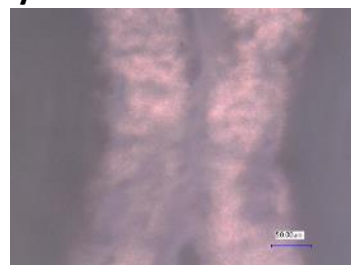
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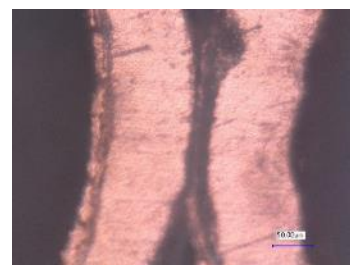
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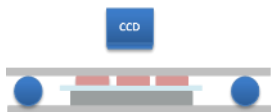
After Stripping

In ether based electrolyte

- Dendrites grow aggressively in carbonate based electrolyte. Dense and uniform Li plating is observed in ether based electrolyte.
- Large amount of dead Li formed in carbonate based electrode after stripping. The plating and stripping in ether based electrolyte is reversible.

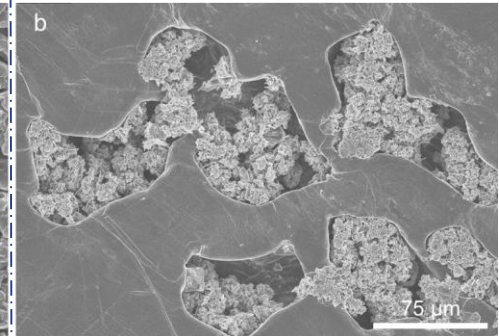
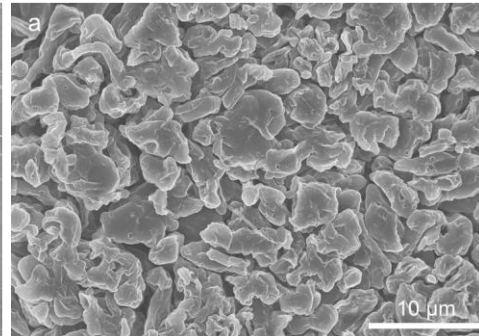
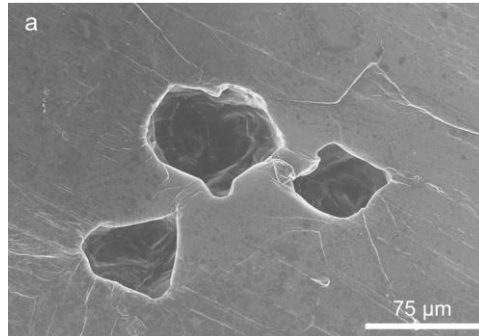


In-situ optical microscope



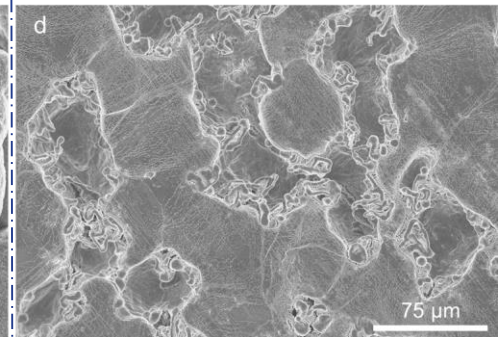
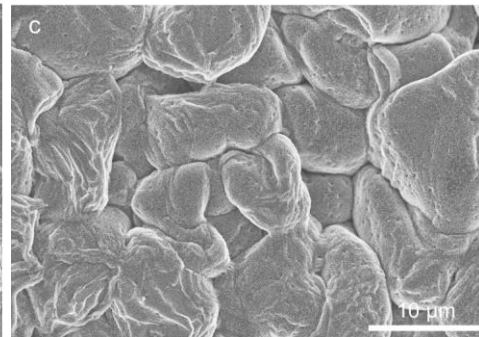
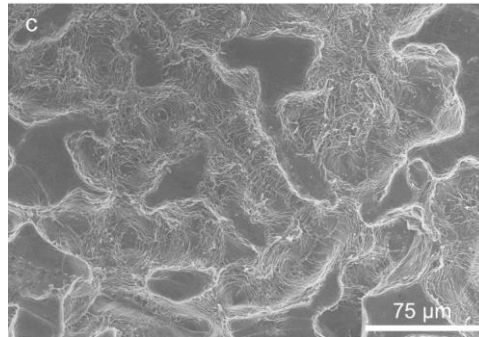
Impact of electrolyte on Li morphology evolution

Carbonate based
electrolyte
(EC-DEC)



Ether based
electrolyte
(DOL-DME)

1 mA cm^{-2}
 4 mAh cm^{-2}



On stripped side

On plated side

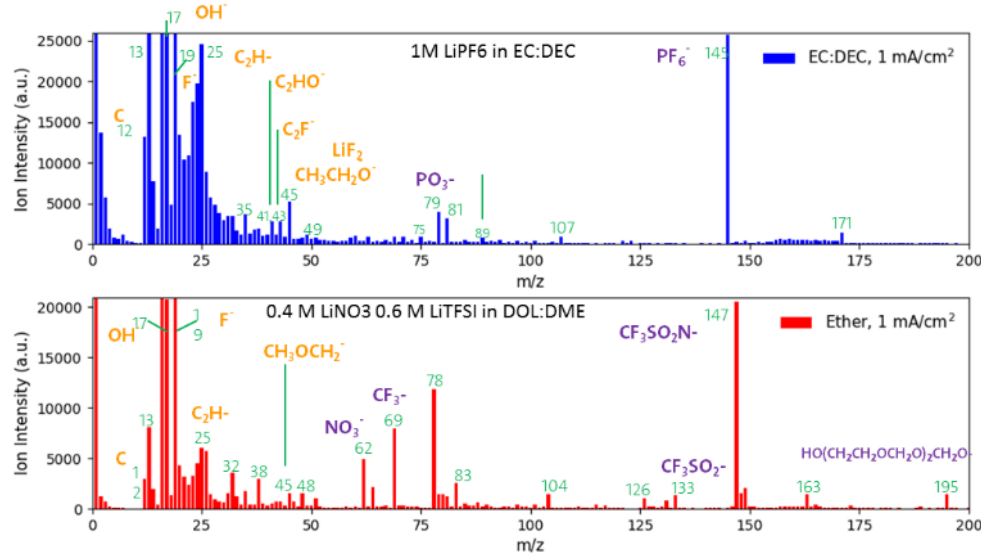
(symmetric cells)

Initial plating on the
stripped side

- Electrolyte plays a critical role in surface morphology evolution during Li plating. More mossy Li forms in carbonate based electrolyte.
- Surface condition is also important for stripping, which impacts the Li plating on the counter side due to localized current distribution.

SEI composition from different electrolytes (TOF-SIMS)

Negative Mode

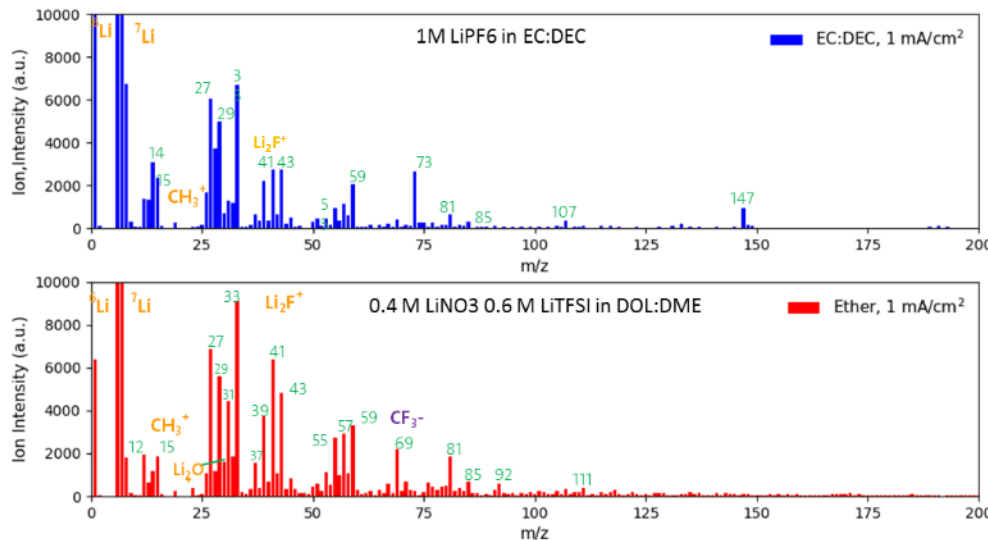


Compounds formed in SEI

- Li₂CO₃
- LiF
- ROCO₂Li
- C-F

- LiF
- Li₂NSO₂CF₃
- LiNO₂
- LiyC₂F_x
- Poly-DOL oligomers

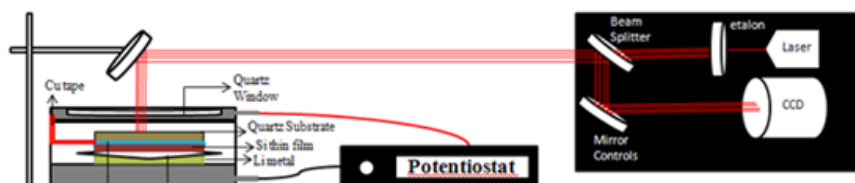
Positive Mode



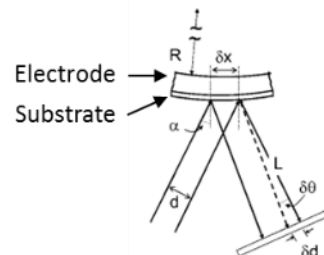
More LiF formed in SEI layer

The decomposition of LiTFSI and DOL in either based electrolyte leads to a robust SEI layer with the inorganic (LiF) inner layer and an elastic organic (Poly-DOL oligomers) outer layer

Accomplishment 3: Identified mechanical response of Li plating and stripping in different electrolytes (Stress evolution, stiffness, and creep behaviors)

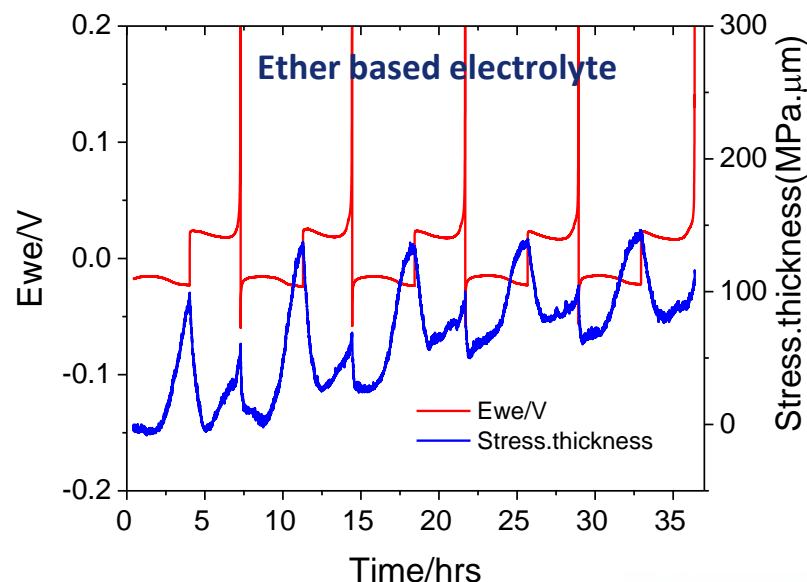
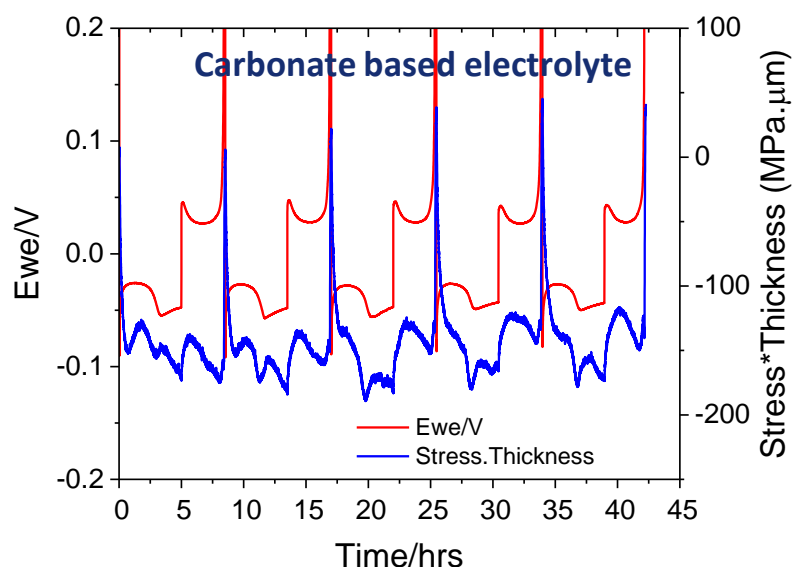


In-situ stress sensor



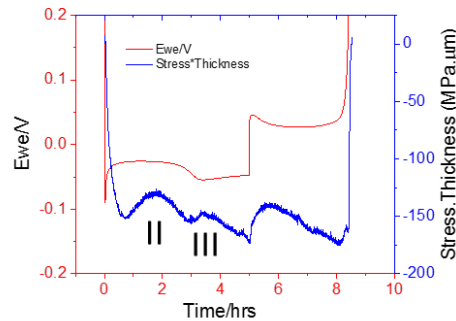
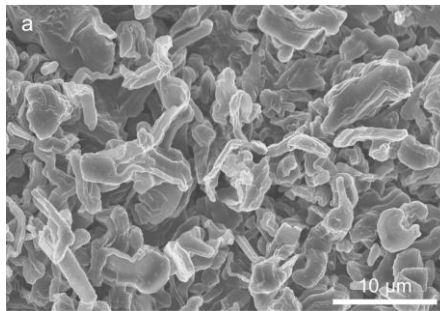
$$\frac{1}{R} = \frac{d - d_0}{d_0} \times \frac{\cos \alpha}{2L} = \kappa$$

$$\langle \sigma \rangle h = \frac{1}{6} M_s H_s^2 \kappa_{st}$$

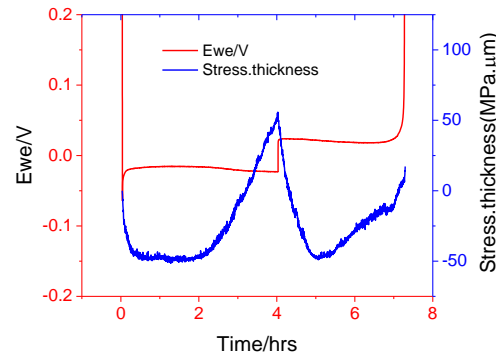
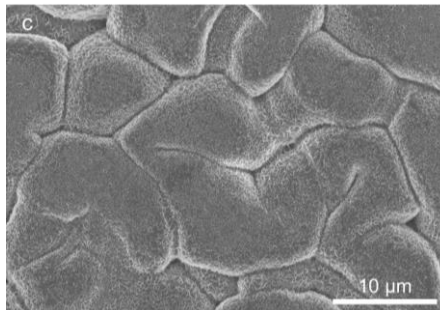
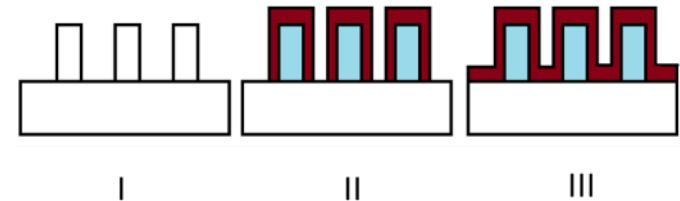


- The compressive stress formed in carbonate based electrolyte likely generates surface wrinkling, leading to an increased surface area and low cycle efficiency.
- The tensile stress in ether based electrolyte tends to smoothen the surface, attributing to better cycle efficiency.

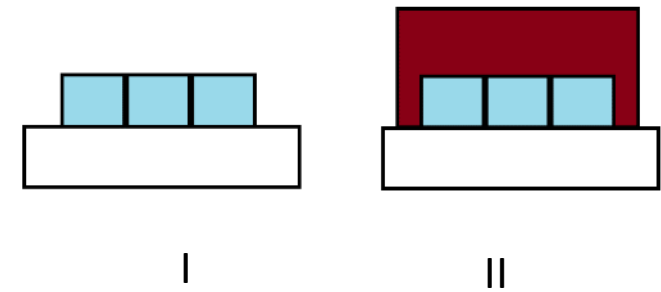
Impact of Li morphology on stress evolution



(a) Carbonate based electrolyte



(b) Ether based electrolyte



- Stress evolution in carbonate based electrolyte is more complicated due to plating and stripping in both mossy and bulk Li.
- The stress level from plating and stripping is comparable to the Li yield strength (<15MPa), which potentially leads to plastic flow of Li during plating and stripping and should be taken into account for electrode design.

Creep behavior of lithium metal (in-situ nanoindentation)

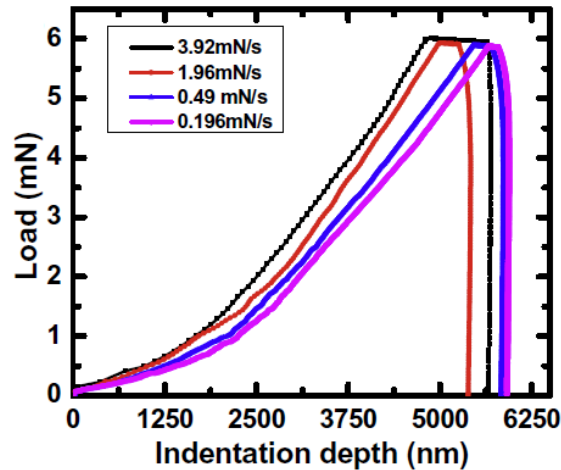
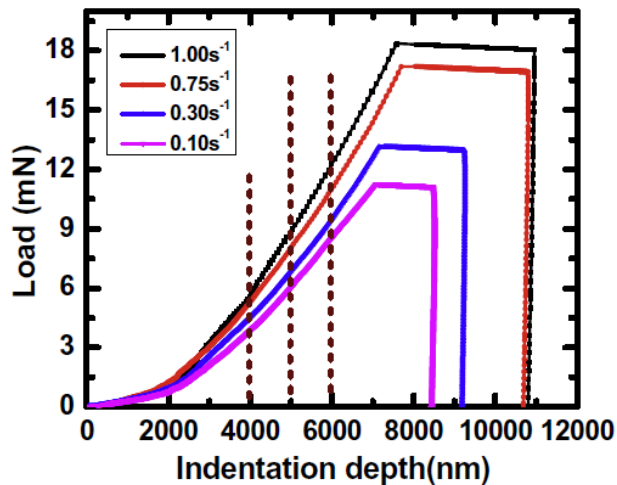
Mechanical behavior

- Constitutive law
- Creep

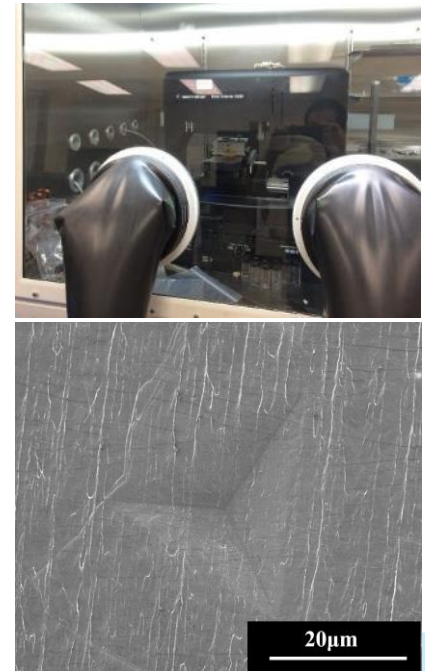


Reliability

- Deformation of lithium caused by pressure in battery cells
- Damage to the separator caused by lithium dendrites
- Pressure and temperature necessary to suppress lithium dendrites

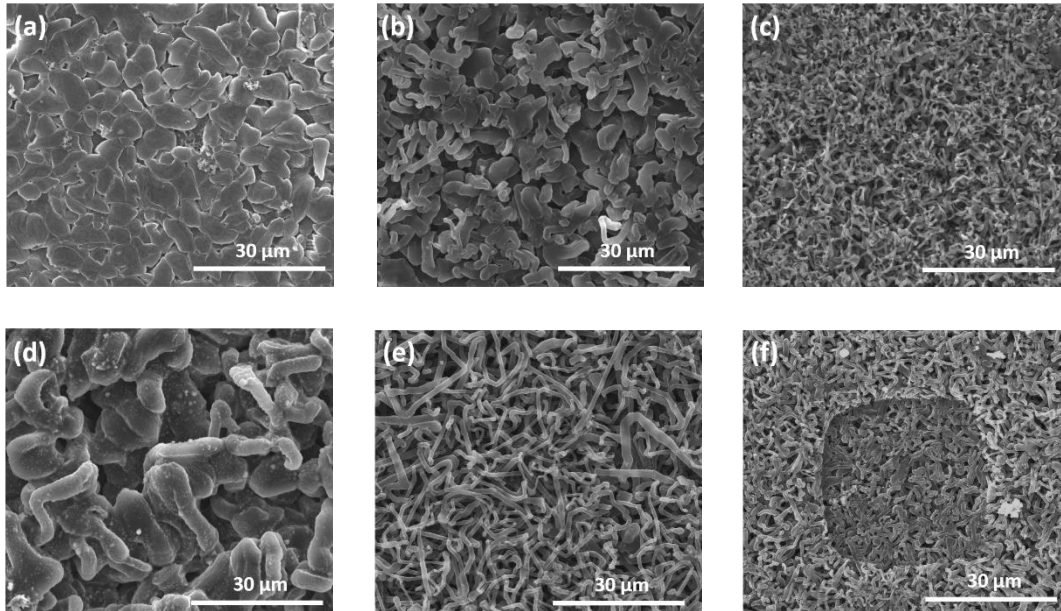


- Rate-dependent deformation suggests creep of lithium at RT.

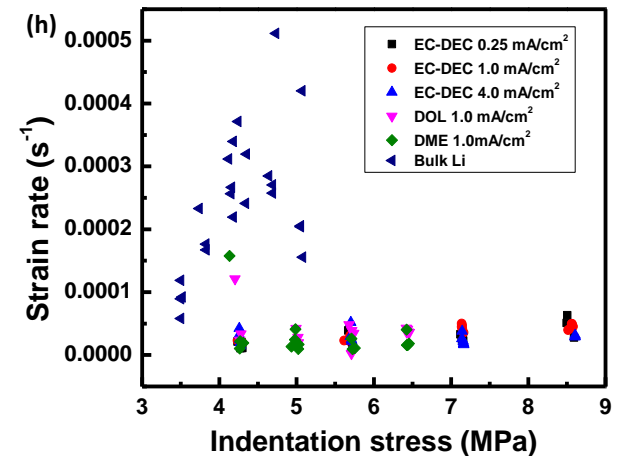
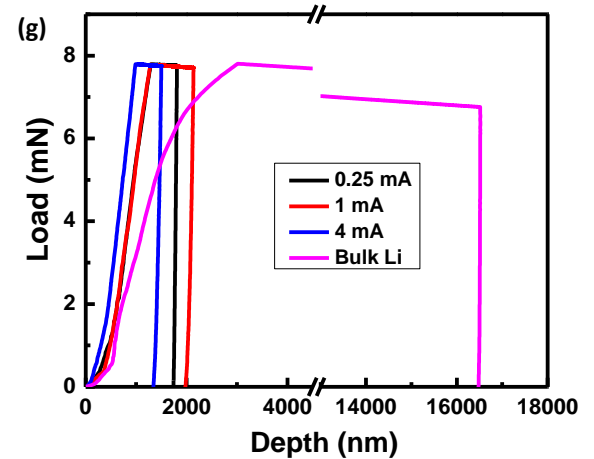


Yikai Wang and Yang-Tse Cheng, Scripta Materialia, 2017, 130: 191-195.

Creep behavior of mossy lithium



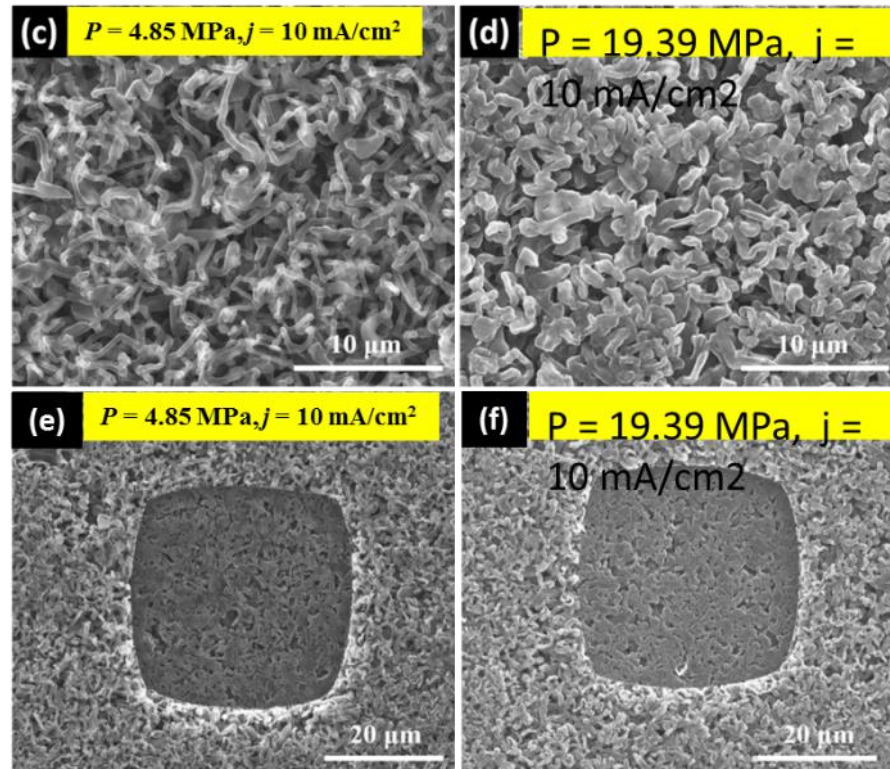
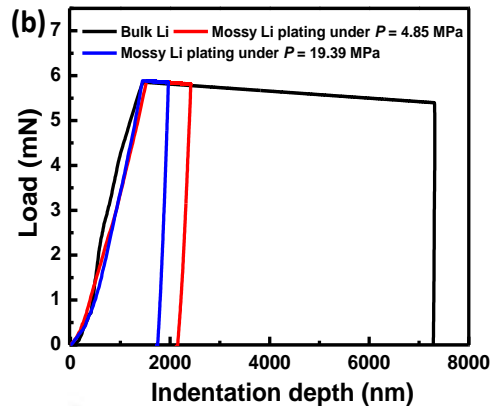
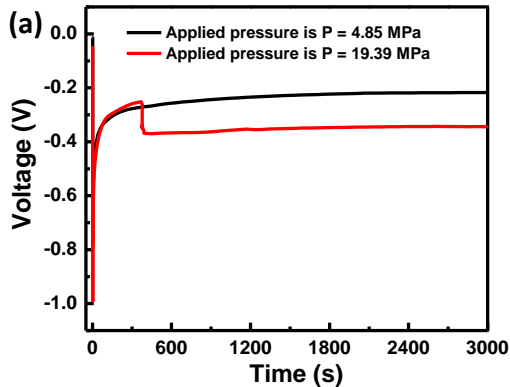
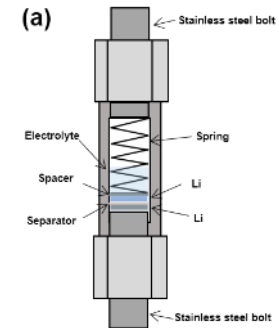
Mossy lithium plated with EC-DEC-based electrolyte at (a) 0.25 mA/cm², (b) 1.0 mA/cm², and (c) 4.0 mA/cm². Mossy lithium plated with (d) DOL-based electrolyte and (e) DME-based electrolyte at 1.0 mA/cm². (f) A typical indent in mossy lithium.



The surface of mossy lithium is “coated” with a thin layer of SEI during the plating process, leading to less plastic flow and higher creep resistance.

Effect of pressure on the morphology, porosity, and mechanical properties of mossy Li

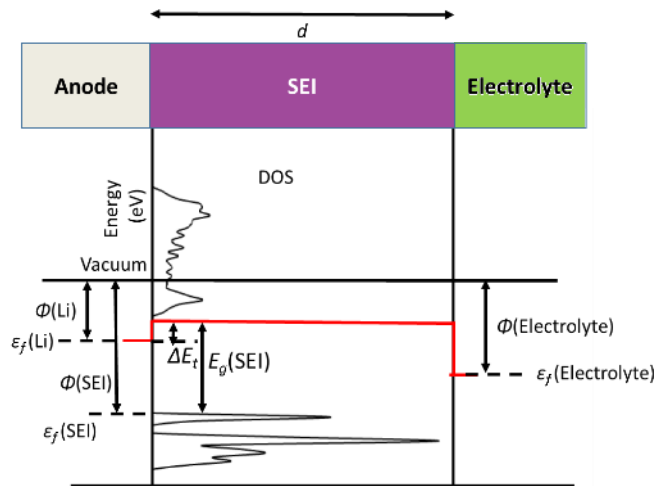
Pressure / MPa	Thickness of mossy Li / μm	Porosity / %
4.85	165	75.76
19.39	77	48.05



- The higher the pressure, the lower the porosity, and the more the creep resistance
- Mossy Li has higher creep resistance than bulk lithium

Accomplishment 4: Identified the critical thickness of electrochemically stable passivation layer on Li

For each component in SEI layer (Li_2CO_3 , LiF , Li_2O , Li_3PO_4), performed DFT calculations. Aligned the work functions (Φ) with respect to vacuum.



Electron tunneling Probability:

$$T = \frac{16\epsilon_f \cdot \Delta E_t}{(\epsilon_f + \Delta E_t)^2} e^{-\frac{4\pi d}{h} \sqrt{2m \cdot \Delta E_t}}$$

Assume a critical thickness, d^* is required to prevent electron tunneling ($T = e^{-40}$).

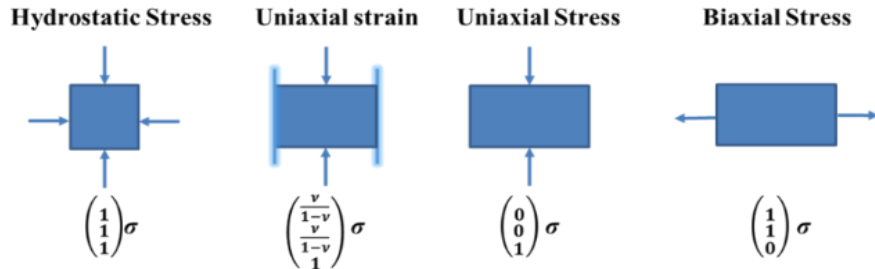
Electron tunneling barrier:

$$\Delta E_t = E_g(\text{SEI}) - \Phi(\text{SEI}) + \Phi(\text{electrode})$$

	GGA		HSE06	
Component	ΔE_t (eV)	d^* (nm)	ΔE_t (eV)	d^* (nm)
Li_2CO_3	1.78	3.02	4.1	2.00
Li_2O	4.15	1.98	4.67	1.87
LiF	3.98	2.03	6.26	1.62
Li_3PO_4	3.49	2.16	5.91	1.66

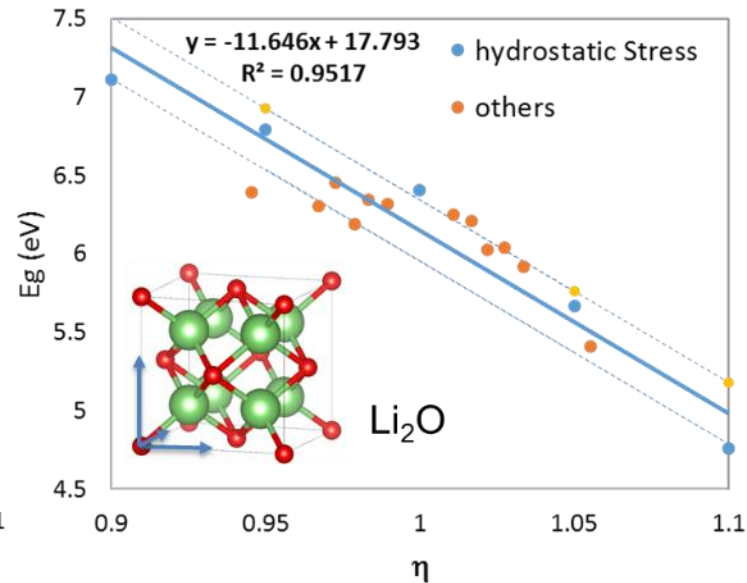
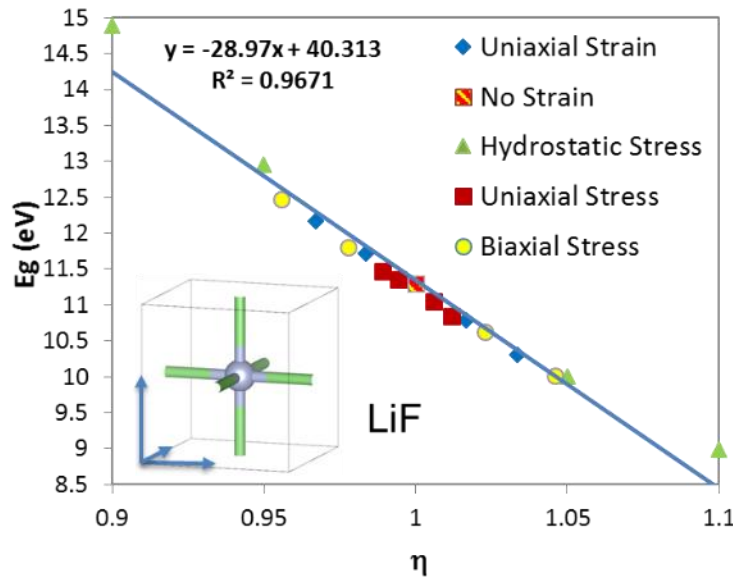
Estimated electron tunneling thickness (2~3 nm)

Mechanical – Electron tunneling coupling effect



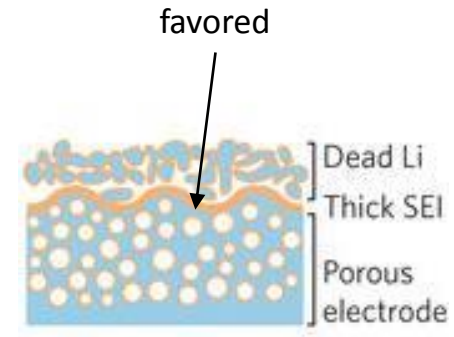
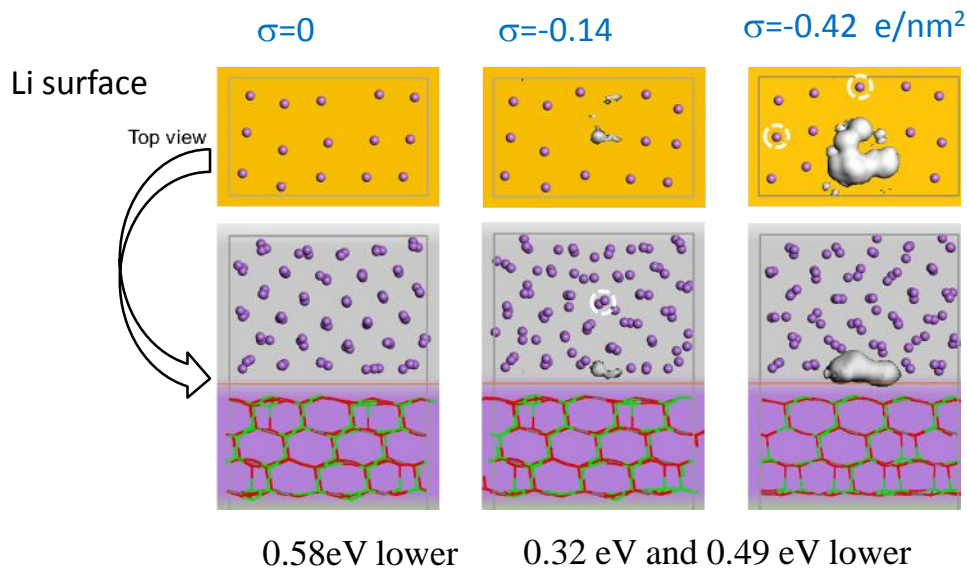
Coupling strain and electron tunneling
 η is defined to characterize the normalized average anion distance

$$\frac{1}{\eta} = \sum \frac{r_0}{r_i}$$



- The band gap (HSE06) changes as a function of average anion distance, η .
- Tunneling barrier ΔE_t decreases under tension, SEI needs to grow thicker to avoid tunneling.

Delithiation generates voids at the Li/SEI interface



*Nature
Nanotechnology* **12**,
194–206 (2017)

Table IV. DFT calculated energetics for different fully-relaxed interfacial supercells.

	Li(001)/Li ₂ CO ₃ (001)	Li(110)/Li ₂ CO ₃ (001)
Formation Energy (10^{-18} J/simulation cell)	1.836	1.926
Interfacial Energy (J/m ²)	0.498	0.573
Work of Adhesion (J/m ²)	0.167	0.124
Strain Energy (mJ/m ³)	52.711	6.248
Strain Energy Contribution (%)	11.73	1.32

- Weak Li/SEI interface
- Void could lead to delamination
- Must be compressed to maintain contacts

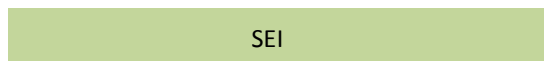
- Interfacial engineering is needed to tailor the current distribution and balance the current density, the kinetics of plating/stripping, and Li diffusion.

Accomplishment 5: Established design criteria to mechanically stabilize SEI layer

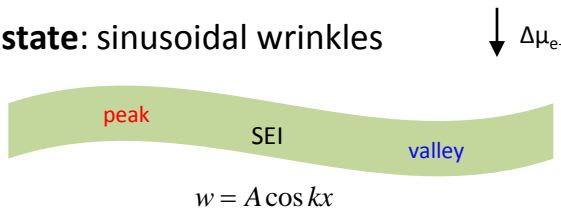
Kinetic model of Li plating and SEI wrinkling on Li metal (surface roughening from fracture mechanics point of view)

Apply Monroe-Newman model to SEI/Li system

Undeformed state: flat, internal compressive stress



Deformed state: sinusoidal wrinkles



curvature

$$\kappa_{\text{peak}} = -k^2 A$$

$$\kappa_{\text{valley}} = k^2 A$$

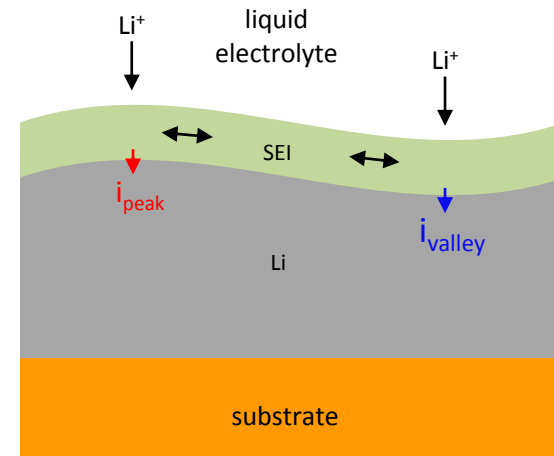
pressure change

$$\Delta p_{\text{peak}} = \frac{1+\nu}{6} \bar{E} h k^2 A \quad \Delta p_{\text{valley}} = -\frac{1+\nu}{6} \bar{E} h k^2 A$$

interfacial normal stress change

$$\Delta \tau_{\text{peak}}^m = -\frac{1+\nu}{6} \bar{E} h k^2 A \quad \Delta \tau_{\text{valley}}^m = \frac{1+\nu}{6} \bar{E} h k^2 A$$

- Li plating resists SEI wrinkling.



The electrochemical potential change of electrons induced by wrinkling

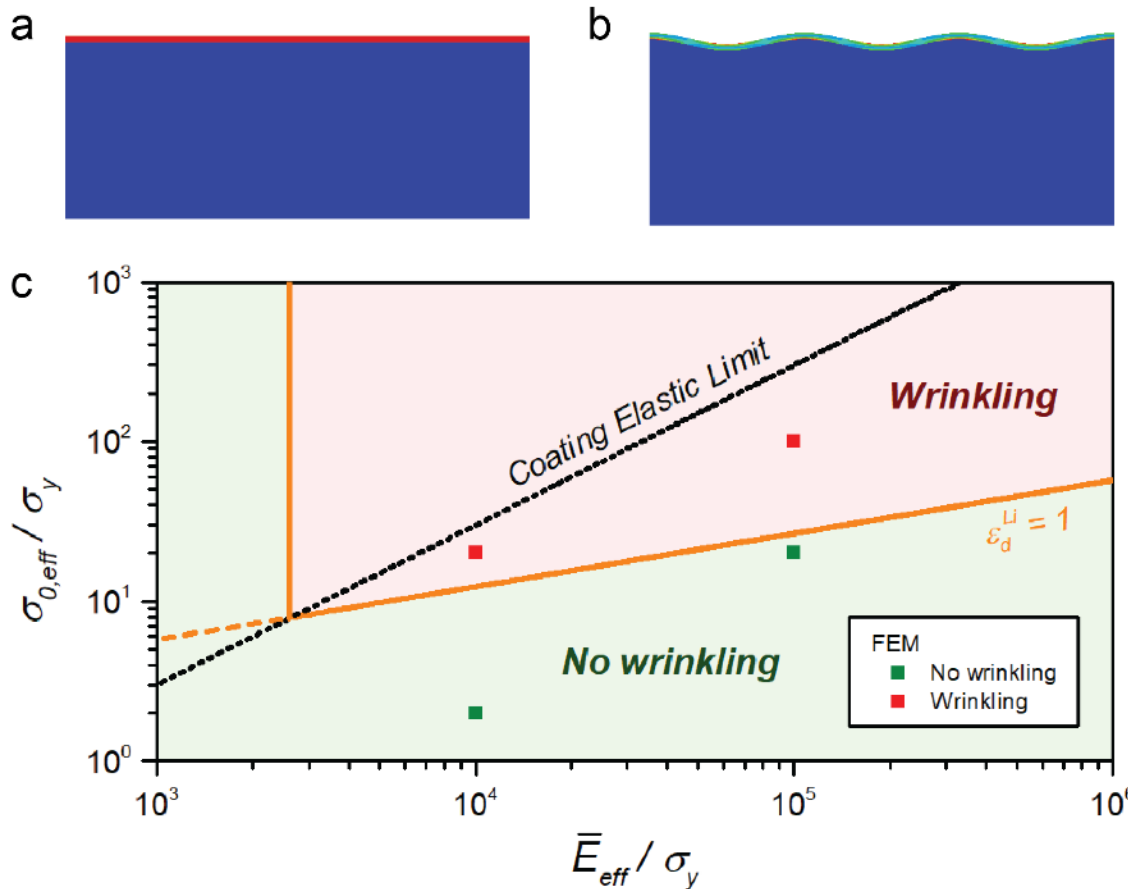
$$\Delta \mu_{\text{peak}} = - \left[\frac{\bar{V}_{\text{Li}} + t_{\text{SEI}}^0 \bar{V}_{\text{SEI}}}{2} \gamma + \frac{t_{\text{SEI}}^0 \bar{V}_{\text{SEI}} E_{\text{SEI}} h_{\text{SEI}}}{6(1-\nu_{\text{SEI}})} \right] k^2 A < 0$$

$$\Delta \mu_{\text{valley}} = \left[\frac{\bar{V}_{\text{Li}} + t_{\text{SEI}}^0 \bar{V}_{\text{SEI}}}{2} \gamma + \frac{t_{\text{SEI}}^0 \bar{V}_{\text{SEI}} E_{\text{SEI}} h_{\text{SEI}}}{6(1-\nu_{\text{SEI}})} \right] k^2 A > 0$$

$$i_{\text{peak}} < i_{\text{valley}}$$



Theoretical and finite element analysis of wrinkling of protective coatings on Li metal electrodes



- (a) a flat coating with a compressive pre-stress;
- (b) a wrinkled coating after Li deposition (only part of the Li metal is shown).
- (c) A wrinkling phase diagram of a thin film coating with different moduli and pre-stresses on a Li metal electrode.

- The elastic limit (black dashed line) of the coating, beyond which plastic yielding occurs, was determined by a maximum elastic strain of 0.3% in the inorganic coating.
- The tensile normal stress at the peaks of the wrinkles could initiate the interfacial delamination between the coating and the Li metal.

Accomplishment 6: Developed protective coatings as artificial SEI layer

Learning from in-situ diagnostic and simulation

1. LiF is a critical component to provide mechanical and electrochemical passivation on Li surface. Polymer matrix helps to accommodate Li volume expansion.
2. Minimizing the surface area not only improves the cycle efficiency, but also facilitates Li plastic flow to relax the mechanical stress.

Learning from literature

1. LiF/polymeric matrix in the SEI layer is compact and stable, beneficial for suppressing Li dendrite growth;
2. Typically, fluoroethylene carbonate (FEC) as electrolyte additive is needed and is consumed with increasing cycle numbers.
3. Gas generation is a potential issue for FEC containing electrolyte.

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Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries

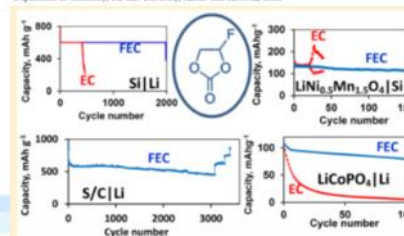
Xue-Qiang Zhang, Xin-Bing Cheng, Xiang Chen, Chong Yan, and Qiang Zhang*

Lithium (Li) metal has been considered as an important substitute for the graphite anode to further boost the energy density of Li-ion batteries. However, Li dendrite growth during Li plating/stripping causes safety concern and poor lifespan of Li metal batteries (LMB). Herein, **fluoroethylene carbonate (FEC) additives are used to form a LiF-rich solid electrolyte interphase (SEI).** The FEC-induced SEI layer is compact and stable, and thus beneficial to obtain a uniform morphology of Li deposits. This uniform and dendrite-free

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Fluoroethylene Carbonate as an Important Component for the Formation of an Effective Solid Electrolyte Interphase on Anodes and Cathodes for Advanced Li-Ion Batteries

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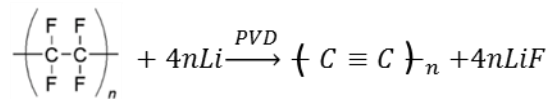
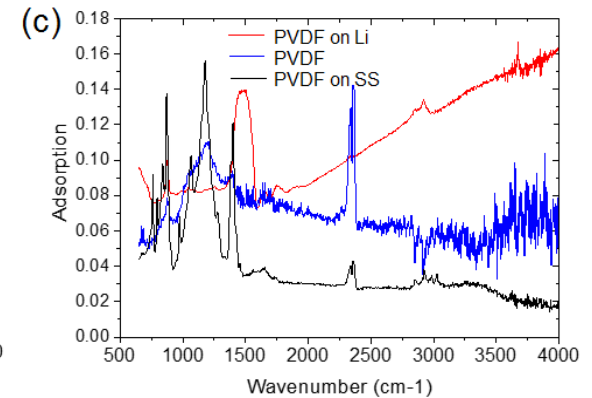
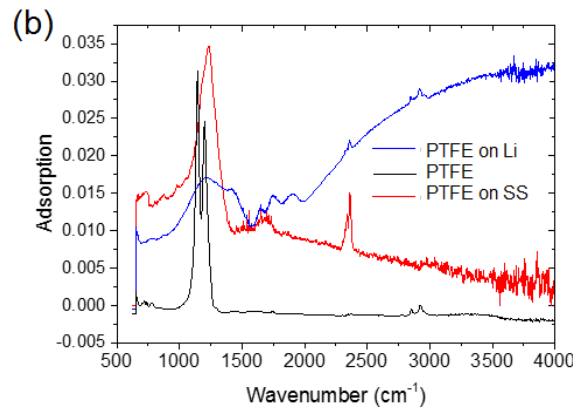
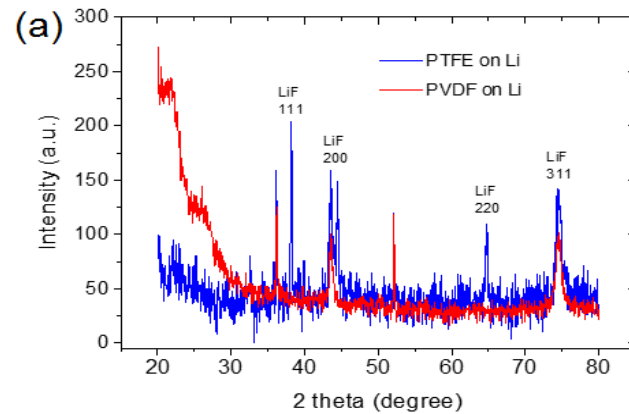
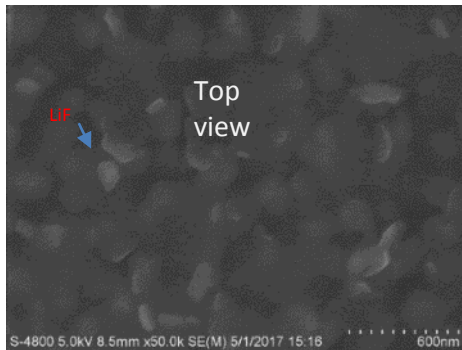
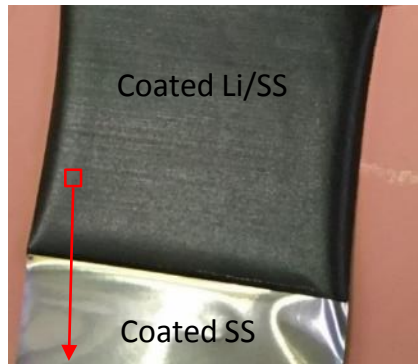


PERSPECTIVE



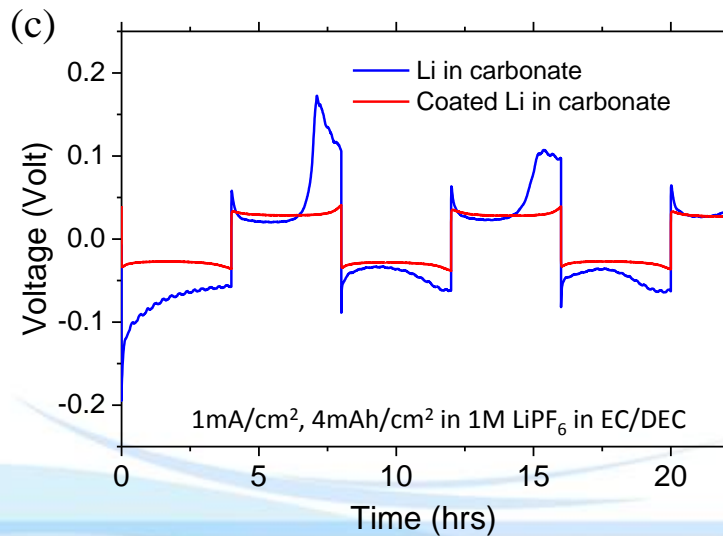
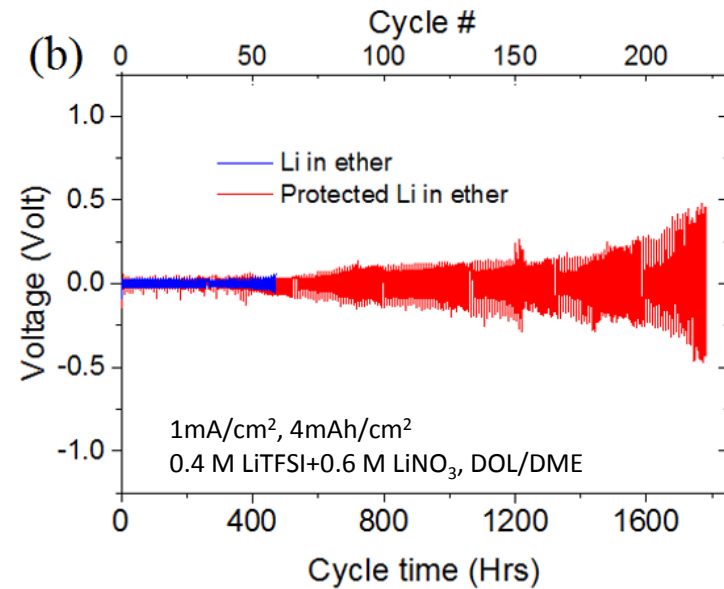
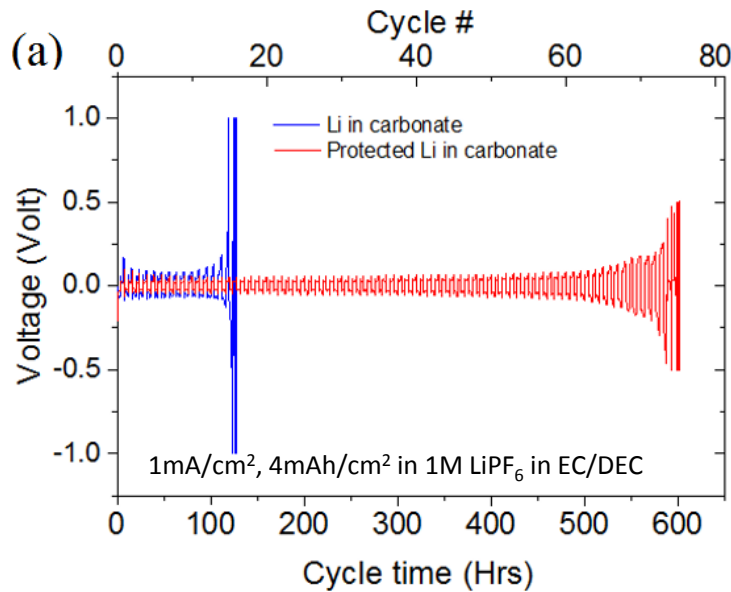
THE WORLD'S BEST VEHICLES

Defluorination-derived Artificial SEI Layer



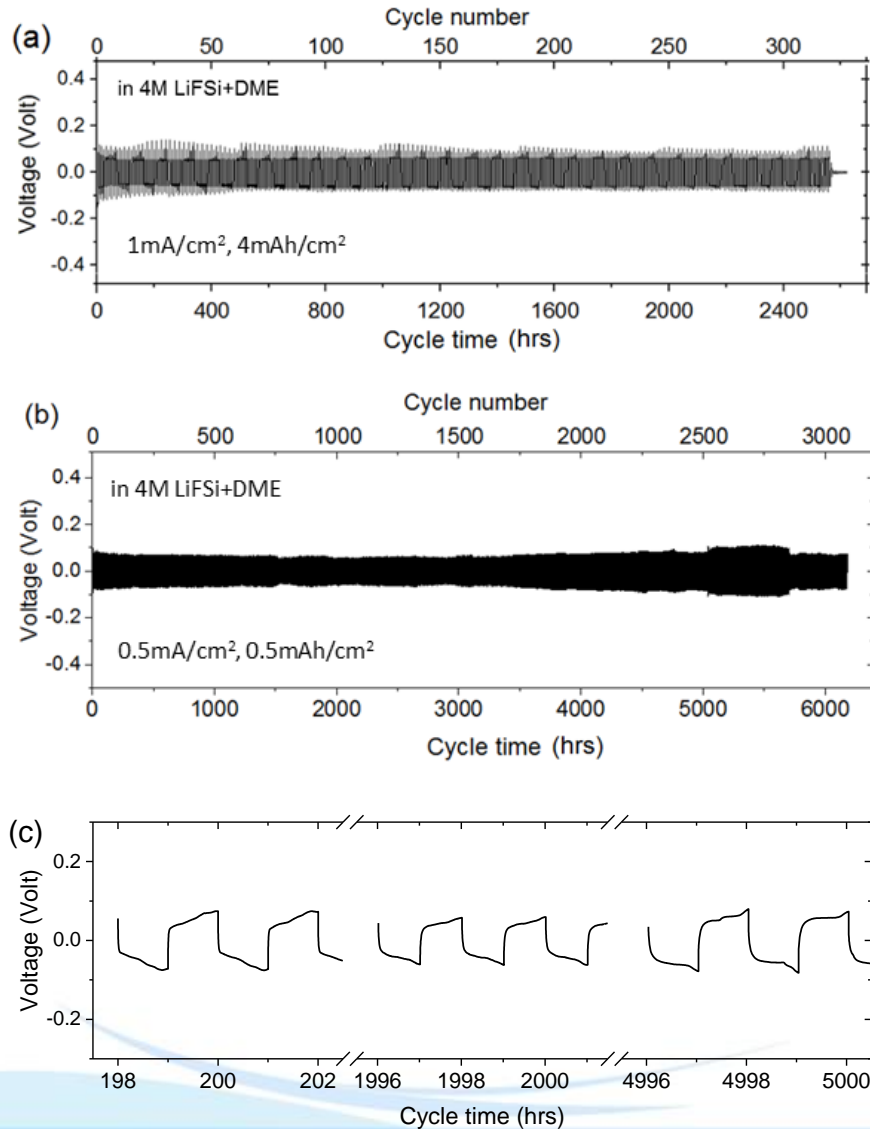
- The defluorination reaction between fluorine based polymers and Li creates a unique nanocomposite layer where nano-sized lithium fluoride crystals are embedded in carbonaceous matrix.

Artificial SEI to protect Li metal



- The defluorination derived artificial SEI layer effectively suppresses the dendrite formation and mossy structure evolution, leading to dramatically increased cycle stability.

Protected electrodes in concentrated electrolyte



Synergistic effect of protective coating and electrolyte leads to promising cycle stability:

- Coating suppresses mossy structure formation
- High concentration electrolyte suppresses the side reaction between solvent and Li, and forms a compacted SEI layer.

High cost (salt), high viscosity

Need further optimization to avoid shorting.

Responses to Previous Year Reviewers' Comments

- New project started on 10/1/2016.
- Not reviewed last year.

Collaborations and Coordination with Other Institutions

Dr. Wanli Yang (LBNL)	Apply advanced synchrotron to understand the failure mechanism of Li metal with different artificial SEI layers;
Dr. Wu Xu Dr. Chongmin Wang, Dr. Jie Xiao (PNNL)	Investigate the stability of artificial SEI on Li using <i>in-situ</i> TEM; Advanced electrolyte additives;
Prof. Zhongwei Chen (U. Waterloo)	Advanced electrode architecture;
Dr. Teddy Huang (Bruker)	In-situ electrochemical AFM and nanomechanics characterization.

Conclusions

- Comprehensive in-situ diagnostic tools have been developed to investigate the coupled mechanical and chemical degradation of SEI/Li.
- By correlating the mechanical behaviors, composition, and cycle efficiency from two typical electrolytes, a promising SEI layer composition and structure has been identified for improving the cycle stability of Li electrodes.
- An artificial SEI layer derived from the defluorination reaction of fluorine based polymers with Li has been developed. The unique nanocomposite coating with LiF crystals embedded in carbonaceous matrix effectively suppresses the dendrite formation and mossy structure evolution, leading to dramatically increased cycle stability.

Remaining challenges and barriers

- Understanding the impact of multi-components in SEI layer on the Li transport and current density distribution along the interface between SEI and Li metal.
- Lack of reliable approach to characterize the interfacial fracture strength between SEI and Li Metal.
- Role of mechanical and electrochemical factors in suppressing the dendrite growth and improving the cycle efficiency. Although the critical thickness of electrochemically stable passivation layer on Li, further effort will be on improving the mechanical stability of the passivation layer.

Future plans

- Link the knowledge obtained from in-situ experiments with the long-term electrochemical tests: Develop isotope exchange and ToF-SIMS approach to trace Li microstructure evolution. The results will be correlated with the SEI mechanical properties to predict desired SEI properties, with special focus on the SEI/Li interface
- Tailor SEI chemistry and perform property predictions at QM and MD levels to investigate structure-chemistry-property relationship of SEI on Li and the impact on Li plating and stripping.
- Further optimize the structural and chemical design of protective coating as artificial SEI, and test the cycle performance in full cell paired with both sulfur and high energy NMC.

Acknowledgements

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